

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
28 June 2001 (28.06.2001)

PCT

(10) International Publication Number
WO 01/46296 A1

- (51) International Patent Classification⁷: C08G 83/00, 63/60, C09D 201/00
- (21) International Application Number: PCT/US00/30556
- (22) International Filing Date:
6 November 2000 (06.11.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
09/470,405 22 December 1999 (22.12.1999) US
- (71) Applicant (*for all designated States except US*): BASF CORPORATION [US/US]; Anne Gerry Sabourin, Patent Department, Mary E. Golota, Patent Department, 26701 Telegraph Road, Southfield, MI 48034-2442 (US).
- (72) Inventor; and
- (75) Inventor/Applicant (*for US only*): RAMESH, Swaminathan [US/US]; 6879 Longwood, Canton, MI 48187 (US).
- (74) Agents: SABOURIN, Anne, Gerry et al.; BASF Corporation, 26701 Telegraph Road, Southfield, MI 48034-2442 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— *With international search report.*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 01/46296 A1

(54) Title: HYPERBRANCHED POLYOL MACROMOLECULE, METHOD OF MAKING SAME, AND COATING COMPOSITION INCLUDING SAME

(57) Abstract: A hyperbranched polyester polyol macromolecule, having a plurality of both embedded and exterior hydroxyl groups thereon, may be synthesized in a 5 polymerization reaction having several steps. The hyperbranched polyol includes a central nucleus, a first chain extension, an inten-nediate substituent and a second chain extension. The central nucleus is a hydrocarbon structure with a plurality of oxygen atoms. The first chain extender is attached to the central nucleus and includes a carboxylic ester group and a plurality of hydroxyl groups. The intermediate substituent is attached to the first chain extender, and is a polyfunctional carboxylic acid or anhydride thereof. The preferred intermediate substituent is a cyclic compound. The second chain extension is attached to the inten-nediate substituent. The preferred second chain extension includes a glycidyl ester or epoxy. Methods of making a hyperbranched polyester polyol are also disclosed. Coating compositions in which the hyperbranched polyol is reacted with an aminoplast or with an isocyanate are also encompassed by the invention.

HYPERBRANCHED POLYOL MACROMOLECULE, METHOD OF MAKING SAME, AND COATING COMPOSITION INCLUDING SAME

BACKGROUND OF THE INVENTION

5 1. Field of the invention

The present invention relates to a hyperbranched polyol macromolecule having both primary and secondary hydroxyl groups as part of the structure thereof, and also including a branched hydrocarbon chain to give flexibility to the polymer. More particularly, the present invention relates to a hyperbranched polyester polyol
10 macromolecule, of the type described, which is usable to form high-solids coating compositions; to a method of making the macromolecule, and to coating compositions made therewith.

2. Description of the Background Art

Certain hyperbranched macromolecules are known for use in preparing high-solids
15 coating compositions.

U.S. patent no. 5,418,301 to Hult et al. teaches a dendritic macromolecule which is formed beginning with a central initiator molecule having reactive hydroxyl groups thereon. A monomeric chain extender is attached to each of the reactive hydroxyl groups to form a highly branched structure. A chain stopper molecule may, optionally, be added to
20 the chain extender to further increase the size of the macromolecule, and to terminate the macromolecule-forming reaction.

U.S. patent no. 5,663,247 to Sorensen et al. discloses another hyperbranched polyester macromolecule, formed from an epoxide nucleus and hydroxy-functional carboxylic acid chain extenders, and a method of making the hyperbranched
25 macromolecule.

Other polyesters are disclosed in U.S. patent numbers 5,852,162 and 5,869,191.

Some coating compositions formed with the known hyperbranched macromolecule have a tendency to crack when they are flexed. Such relatively brittle materials are less than optimal for use in making coating compositions which are intended to be applied to automotive bodies or flexible materials, such as resiliently bendable plastics or elastomers.

- 5 Since modern engineering often combines dissimilar materials such as, e.g., metal and plastics or elastomers into an assembled product to be painted, a need exists for coatings which are useful to paint all of such dissimilar materials.

Although the known hyperbranched macromolecules are useful for their intended purposes, a need still exists in the art for an improved hyperbranched macromolecule
10 having engineered properties which allow formation of coating compositions which are both durable and flexibly resilient.

SUMMARY OF THE INVENTION

The present invention provides a hyperbranched polyester polyol macromolecule having a plurality of both embedded and exterior hydroxyl groups with a branched
15 hydrocarbon chain for flexibility thereon.

A hyperbranched polyol in accordance with the invention, generally, includes

a) a central nucleus comprising a hydrocarbon structure with a plurality of oxygen atoms;

b) a first chain extension attached to the central nucleus, the first chain extension
20 being formed from a compound comprising a carboxyl group and a plurality of hydroxyl groups;

c) an intermediate substituent attached to the first chain extension, the intermediate substituent being formed from a compound selected from the group consisting of polyfunctional carboxylic anhydrides and acids thereof; and

25 d) a second chain extension attached to the intermediate substituent, the second

chain extension comprising a hydroxyl group and being formed from a flexible hydrocarbon compound having a terminal or non-terminal epoxide group thereon.

A particularly preferred starter polyol for use in the present invention is trimethylol propane. A preferred intermediate substituent for attaching to the first chain extension is a cyclic anhydride or acid thereof, most preferably an alicyclic anhydride or acid.

The present invention also encompasses a method of making a hyperbranched polyester polyol. A method in accordance with the invention, generally, includes the steps of:

- a) reacting a polyol with a first chain extender, which contains a plurality of hydroxyl groups and also contains a carboxyl group, to form a first generation branched core;
- b) optionally, further reacting the first generation branched core with the first chain extender, to form a subsequent generation branched core;
- c) reacting the first or subsequent generation branched core with a compound selected from the group consisting of carboxylic anhydrides and acids to form an ester bridge therewith, thereby forming an intermediate polyester macromolecule; and
- d) reacting the intermediate polyester macromolecule with a second chain extender having a terminal or non-terminal epoxide group in a flexible hydrocarbon chain thereon, to form a hyperbranched polyol having both primary and secondary hydroxyl groups thereon.

Hyperbranched polyols which are products of the above method exhibit the low viscosity needed for coatings operations.

Accordingly, it is an object of the present invention to provide a method of making a hyperbranched polyester polyol having both exterior (primary) and partially embedded (secondary) hydroxyl groups in the structure thereof.

For a more complete understanding of the present invention, the reader is referred to the following detailed description section and the Examples set out therein.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention provides a hyperbranched polyester polyol macromolecule
5 having a plurality of primary, or exterior hydroxyl groups thereon, and also having a plurality of secondary, or embedded hydroxyl groups.

As used throughout the present specification, the term "primary hydroxyl group" is intended to mean a hydroxyl group located at or near the outer periphery of the hyperbranched molecule, so as to be relatively accessible for reaction, and the term
10 "secondary hydroxyl group" is intended to mean a hydroxyl group which is located deeper in the branched structure than the outer periphery, that is, which is at least partially embedded in the macromolecule.

While not wishing to be bound by any theory, it is believed that this dual level of hydroxyl groups in the macromolecule with the hydrocarbon chain from the second
15 extension, when the polyol hereof is used in a coating composition, contributes to both hardness and flexibility of the finished coating composition. Also, depending on the ratios of the primary to the secondary hydroxyls present, the final properties of the coating can be tailored to suit the needs of the application.

A hyperbranched polyol in accordance with the invention, generally, includes:

- 20 a) a central nucleus comprising a hydrocarbon structure with a plurality of oxygen atoms;
- b) a first chain extension attached to the central nucleus, the first chain extension being formed from a compound comprising a carboxyl group and a plurality of hydroxyl groups;
- 25 c) an intermediate substituent attached to the first chain extension, the intermediate

substituent being formed from a compound selected from the group consisting of polyfunctional carboxylic anhydrides and acids thereof; and

- d) a second chain extension attached to the intermediate substituent, the second chain extension being formed from a flexible hydrocarbon compound having a terminal or non-terminal epoxide group thereon.

Preferably, the hyperbranched polyol macromolecule hereof has a plurality of primary hydroxyl groups and a plurality of secondary hydroxyl groups thereon.

Method of Making the Polyol

The present invention also encompasses a method of making a hyperbranched polyester polyol. A method in accordance with the invention, generally, includes a first step of reacting a starter polyol with a first chain extender, which contains a plurality of hydroxyl groups and also contains a carboxyl group, to form a first generation branched core.

In this first step, preferred starter polyols are those having two or more reactive hydroxyl groups thereon. Diols such as ethylene glycol, propylene glycol, dimethylolpropionic acid and related structures may be used as starter polyols. Triols such as glycerol, trimethylol propane, trimethylol butane and related structures are favored, although compounds having four hydroxyl groups thereon, such as pentaerythritol, may also be used as starter polyols. A particularly preferred starter polyol, for use in forming the central core, is trimethylol propane (TMP).

Also in the first step, materials usable as the first chain extender include carboxylic acids having two or more hydroxyl groups thereon, as well as carboxylic acids of the type described in which one or more of the hydroxyl groups have been hydroxyalkyl substituted. A particularly preferred material for use as the first chain extender is dimethylol propionic acid (DMPA).

A conventional esterification catalyst may be used in this first step, if desired, such as sulfuric acid, dibutyltin oxide or other known catalyst.

Optionally, this first generation branched core may be further reacted with the first chain extender, or with another different monomer having a similar structure as described
5 above in connection with the first chain extender, one or more additional times, as desired, to cause further branching and growth thereof. Such additional polymerization of the first generation branched core, where used, forms a second, third, fourth, or higher generation branched core, as desired, and according to the particular needs under consideration.

The next step in the method of forming the hyperbranched macromolecule hereof
10 involves reacting the branched core, at whatever level of generational branching is used, with an intermediate substituent which includes a polyfunctional carboxylic anhydride or acid thereof, to form an intermediate polyester macromolecule having reactive carboxyl groups thereon. The intermediate substituent may be selected from, e.g., phthalic acid, isophthalic acid, orthophthalic anhydride, tetrahydrophthalic anhydride,
15 hexahydrophthalic anhydride, trimellitic anhydride, succinic anhydride and similar such compounds. Preferred materials for use as the intermediate compound are cyclic polyfunctional carboxylic anhydrides. Particularly preferred materials, for use as the intermediate substituent, are hexahydrophthalic anhydride (HHPA) and methyl, hexahydrophthalic anhydride.

20 The next step in the method of forming the hyperbranched polyol macromolecule hereof involves reacting the intermediate polyester macromolecule with a second chain extender to form a hyperbranched polyol macromolecule having both primary and secondary hydroxyl groups thereon.

The second chain extender is a flexible hydrocarbon compound having a terminal
25 or non-terminal epoxide group thereon. The second chain extender may be selected from

the group consisting of glycidyl esters, glycidyl ethers, epoxides, epoxy resins, epoxidized acids, and epoxidized alcohols. Preferably, the second chain extender is selected from the group consisting of glycidyl esters and glycidyl ethers.

Some examples of possible compounds usable as the second chain extender include
5 cyclohexane oxide, any aliphatic chain with terminal or non-terminal epoxide group such as, for example, cis 2, 3-epoxybutane, 1-2-epoxybutane, 1-2-epoxyhexane, 1-2-epoxyoctane, 1-2-epoxydecane, cis-7, 8-epoxy-2-methyloctadecane, hexafluoropropylene oxide, and the glycidyl esters sold by the Shell Chemical company under the trademark "Cardura". The above list is intended to be illustrative rather than limitative. Those skilled in the art will
10 realize that many other compounds may be used. Coating Compositions Incorporating the Hyperbranched Polyol The present invention also relates to coating compositions made using the hyperbranched macromolecule hereof. In particular, the hyperbranched polyol hereof is suitable for use in preparing clear topcoat compositions.

In formulating these coating compositions, the macromolecule with the dual levels
15 of hydroxyl groups thereon may be reacted with an aminoplast curing agent, or may be reacted with an isocyanate or isocyanurate, or may be reacted with combinations of aminoplasts and isocyanates and/or isocyanurates. Also, if some of the carboxylic acids are incorporated into the structure of the macromolecule and are left free, they can be used to cross-link with polyepoxides to form a flexible coating.

20 The cross-linkers can be drawn from a list of known melamine-formaldehyde resins, isocyanates and isocyanurates and polyepoxides. The list would include, and is not restricted to, compounds like Cymel-303, fully methylated hexamethoxymethylmelamine, partially methylated methoxymethylmelamine, butoxymethylmelamines, butoxy, methoxymethylmelamines, hexamethylenediisocyanate(HDI),
25 isophoronediiisocyanate(IPDI), cyclohexanediisocyanate(CHDI),

toluenediisocyanate(TDI), methylenediphenylenediisocyanate (MDI), the isocyanurates derived from HDI, IPDI,CHDI, TDI, MDI, epoxides from the EPON series sold by the Shell Chemical company, bis-phenol A type epoxides, acrylic polymers with glycidylacrylate or methacrylate as one of the monomers. Other ingredients that go into making the paint are well known to those knowledgeable in the art and would include flow additives for rheology control and leveling, solvents, catalysts.

When the curing takes place by reacting the hydroxyl groups of the hyper-branched compounds, either melamine-formaldehyde resins or isocyanates/isocyanurates can be used by themselves or combinations of them may be used. Likewise, the carboxylic acids can be cured with polyepoxides either by themselves or can have additional curing perpetuated by melamine-formaldehyde or isocyanates/ isocyanurates. The ratios of cross-linkers to the reacting groups can be between 2 – 0.1, preferably between 1.2 – 0.8, based on their equivalent weights. When both primary and secondary hydroxyls are present, the amounts of cross-linkers can be varied such that all the primary hydroxyls will react leaving the secondary hydroxyls free for adhesion purposes, or a fraction of these also reacted to give better humidity resistance.

In general, it has been found that with a dual cure (hydroxyls with melamine-formaldehyde and isocyanates or isocyanaurates, or carboxylic acids with epoxides and hydroxyls with melamine-formaldehyde or isocyanates or isocyanaurates), the resulting film exhibited excellent etch characteristics.

EXAMPLES

The following examples are intended to illustrate, and not to limit the application of the invention. In the following examples, all parts are by weight of the total composition, unless otherwise specified.

RESIN EXAMPLE 1

Referring to the illustrated example in the diagram of Figure 1, a starter polyol 10, shown as a molecule of TMP, is reacted with three molecules of a first chain extender 12, DMPA, in the presence of a sulfuric acid catalyst, to form a first generation branched core 14. As referred to above, this process of reaction with the first chain extender 12 may be repeated as desired, to form a second or higher generation branched core (not shown).

Then, the branched core 14 is reacted with a suitable number of moles of an intermediate reactant 16 which is a polyfunctional carboxylic anhydride or acid thereof, to form an intermediate polyester macromolecule 20 having reactive carboxyl groups thereon. In the example of Figure 1, the intermediate reactant 16 is hexahydrophthalic anhydride (HHPA). The intermediate reactant 16 forms an intermediate substituent in the final hyperbranched macromolecule product.

The intermediate reactant 16 reacts with selected hydroxyl groups of the branched core 14, while leaving other hydroxyl groups on the core unreacted. This is an important aspect of the present invention, and therefore an excess of the intermediate reactant 16 is disfavored. The reaction between the branched core 14 and the intermediate reactant 16 forms an intermediate polyester macromolecule 20 having a plurality of reactive carboxyl groups thereon.

Finally, the intermediate polyester macromolecule 20 is further reacted with a second chain extender 22 which, in this example, is a compound having a terminal epoxide group and a flexible hydrocarbon chain thereon, to form the hyperbranched polyol 24 of the invention, which has both primary and secondary hydroxyl groups thereon.

In the depicted embodiment, this second chain extender 22 is a branched glycidyl ester sold by the Shell Chemical company as CARDURA E-10. In the illustration of Figure 1, R_1 represents the base structure of the intermediate polyester macromolecule, which is symbolized to avoid the necessity of continually redrawing the structure thereof,

and R₂, R₃, and R₄, respectively, represent small alkyl groups. In this example, the epoxide ring of the glycidyl ester 22 is opened, and the oxygen molecule thereof is converted to a hydroxyl group. Again, by choosing not to react all the carboxylic acids with the epoxide, a molecule containing primary and secondary hydroxyl groups along with carboxylic acids
5 can be obtained.

In the example of Figure 1, the polyester was formulated according to the following table.

Table 1

	TMP	1 mole
10	DMPA	3 moles
	HHPA	3 moles
	CARDURA E-10*	3 moles

*(CARDURA is a trademark of the Shell Chemical company.)

67 grams of trimethylol propane was charged into a reaction flask equipped with a
15 stirrer, along with 201 grams of dimethylol propionic acid and 0.2 grams of sulfuric acid as a catalyst. The temperature was raised, to 140 degrees C, over a 45 minute period. A stream of nitrogen was used to help remove the water formed during the condensation reaction. A vacuum pump was connected to the flask at the end of the reaction to complete the removal of the water of the condensation reaction.

20 This reaction resulted in the synthesis of a first generation branched core 14.

Then, 231 grams of HHPA was added and was heated to 140° C and the reaction was monitored by IR equipment for the disappearance of the anhydride peak. This resulted in the formation of an intermediate polyester macromolecule 20. 50 grams of Aromatic 100 were added to adjust the viscosity of the product.

25 When this reaction was complete, 342 grams of CARDURA E-10 were added and

the temperature kept at 140°C. Again, the reaction was followed by the epoxide peak in IR monitoring equipment. Completion of the reaction resulted in formation of the hyperbranched polyol macromolecule 24, which has three primary hydroxyl groups, three secondary hydroxyl groups and no carboxyl groups.

5 RESIN EXAMPLE 2

A polyester was formulated according to the following table.

Table 2

	TMP	1 mole
	DMPA	3 moles
10	HHPA	4 moles
	CARDURA E-10	2 moles

As described in Example 1, 67 grams of TMP and 201 grams of DMPA were reacted in presence of dibutyltin oxide (0.1g) to form the first generation branched core 14. This, in
15 turn, was reacted with 308 grams of hexahydrophthalic anhydride at 140° C, followed by reaction with 228 grams of Cardura E10 at 140° C. As before, the reactions were monitored for completion by IR equipment. This gave a hyper-branched polyol with two primary hydroxyl groups, two secondary hydroxyl groups and two carboxylic acid groups.

RESIN EXAMPLE 3:

20 A polyester was formulated according to the following table.

Table 3

	TMP	1 mole
	DMPA	3 moles
	MHHPA	2 moles
25	CARDURA E-10	2 moles

As described in Example 1, 67 grams of TMP and 201 grams of DMPA were reacted in presence of dibutyltin oxide (0.1g) to form the first generation branched core 14. This, in turn, was reacted with 168 grams of methyl, hexahydrophthalic anhydride at 140° C, followed by reaction with 228 grams of Cardura E10 at 140° C. As before, the reactions were monitored for completion by IR equipment. This gave a hyper-branched polyol with four primary hydroxyl groups, two secondary hydroxyl groups and no carboxylic acid groups.

RESIN EXAMPLE 4:

A polyester was formulated according to the following table.

10

Table 4

TMP	1 mole
DMPA	6 moles
MHHPA	6 moles
CARDURA E-10	4 moles

15

As described in Example 1, 67 grams of TMP and 201 grams of DMPA were reacted in presence of dibutyltin oxide (0.1g) to form the first generation branched core 14. This, in turn, was reacted with 201 grams of DMPA to get a second generation branched core containing twelve primary hydroxyl groups. This, in turn was reacted with 504 grams of methyl, hexahydrophthalic anhydride at 140° C, followed by reaction with 456 grams of Cardura E10 at 140° C. As before, the reactions were monitored for completion by IR equipment. This gave a hyper-branched polyol with six primary hydroxyl groups, four secondary hydroxyl groups and two carboxylic acid groups.

20

PAINT EXAMPLE 1:

36 grams of resin from Example 1 were mixed with 10 grams of

25

hexamethoxymethylmelamine (HMMM) at ambient pressure in an open container at room temperature, with 0.2 grams of dodecylbenzene sulfonic acid (DDBSA) as a catalyst. The reactants were mixed using a stirrer, and Aromatic 100 was used as a solvent to adjust the viscosity. The resultant mixture was drawn down on a metal plate substrate to make a thin clear coat test sample. The film was cured for 30 minutes at 250 degrees Fahrenheit, and subsequently passed an MEK double rub test of over 200.

PAINT EXAMPLE 2:

36 grams of resin from Example 1 were mixed with 19.5 grams of BASF HDI triisocyanate at ambient pressure in an open container at room temperature, with 0.2 grams of dibutyl tin dilaurate as a catalyst. The reactants were mixed using a stirrer, and Aromatic 100 was used as a solvent to adjust the viscosity. The resultant mixture was drawn down on a metal plate substrate to make a thin clear coat test sample. The film was cured for 30 minutes at 250 degrees Fahrenheit, and subsequently passed an MEK double rub test of over 100.

Although the present invention has been described herein with respect to a preferred embodiment thereof, the foregoing description is intended to be illustrative, and not restrictive. Those skilled in the art will realize that many modifications of the preferred embodiment could be made which would be operable. All such modifications which are within the scope of the claims are intended to be within the scope and spirit of the present invention.

CLAIMS

1. A hyperbranched polyol macromolecule, comprising:
 - a) a central nucleus comprising a hydrocarbon structure with a plurality of oxygen atoms;
 - 5 b) a first chain extension attached to the central nucleus, the first chain extension being formed from a compound comprising a carboxyl group and a plurality of hydroxyl groups;
 - c) an intermediate substituent attached to the first chain extension, said intermediate substituent being formed from a compound selected from the group
 - 10 consisting of polyfunctional carboxylic acids and anhydrides thereof; and
 - d) a second chain extension attached to the intermediate substituent, said second chain extension being formed from a compound having a terminal epoxide group thereon.
2. The macromolecule of claim 1, wherein said macromolecule has a plurality of primary
- 15 hydroxyl groups and a plurality of secondary hydroxyl groups thereon.
3. The macromolecule of claim 1, wherein the second chain extension is formed from a compound selected from the group consisting of glycidyl esters, glycidyl ethers, epoxides, epoxy resins, epoxidized acids, epoxidized alcohols, cyclohexane oxide, and aliphatic
- 20 chains having a terminal or non-terminal epoxide group thereon.
4. The macromolecule of claim 1, wherein the second chain extension is formed from a compound selected from the group consisting of cis 2, 3-epoxybutane, 1-2-epoxybutane, 1-2-epoxyhexane, 1-2-epoxyoctane, 1-2-epoxydecane, cis-7, 8-epoxy-2-methyloctadecane,
- 25 and hexafluoropropylene oxide.

5. The macromolecule of claim 3, wherein the second chain extension is formed from a compound selected from the group consisting of glycidyl esters and glycidyl ethers.

5 6. A method of making a hyperbranched polyol macromolecule, comprising the steps of:

a) reacting a starter polyol with a first chain extender which contains a plurality of hydroxyl groups and which also contains a carboxyl group, to form a first generation branched core;

b) optionally, further reacting the first generation branched core with a first chain
10 extender to form a subsequent generation branched core;

c) reacting the first or subsequent generation branched core with a controlled amount of an intermediate reactant selected from the group consisting of carboxylic acids and anhydrides to form an ester bridge therewith, thereby forming an intermediate polyester macromolecule; and

15 d) reacting the intermediate polyester macromolecule with a second chain extender having a terminal epoxide group thereon, to form a hyperbranched polyol having both primary and secondary hydroxyl groups thereon.

7. The method of claim 6, wherein the first generation branched cored is reacted with
20 a first chain extender to form a subsequent generation branched core.

8. The method of claim 6, wherein said intermediate reactant is selected from the group consisting of phthalic acid, isophthalic acid, orthophthalic anhydride, tetrahydrophthalic anhydride, and hexahydrophthalic anhydride.

9. The method of Claim 6, wherein said intermediate reactant is hexahydrophthalic acid or the anhydride thereof.

10. The method of claim 6, wherein said starter polyol is trimethylolpropane.

5

11. The method of claim 6, wherein said first chain extender is dimethylol propionic acid.

12. The method of claim 6, wherein said second chain extender is a glycidyl ester having from 5 to 13 carbon atoms and having a branched structure.

10

13. A hyperbranched polyol macromolecule which is a product of the method of claim 6.

14. A coating composition comprising a reaction product of the macromolecule of claim 1 and an isocyanate.

15

15. A coating composition comprising a reaction product of the macromolecule of claim 1 and an aminoplast.

20

16. A coating composition comprising a reaction product of the macromolecule of claim 1 with an aminoplast, and also with a compound selected from the group consisting of isocyanates and isocyanaurates.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/30556

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G83/00 C08G63/60 C09D201/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 93 17060 A (PERSTORP AB) 2 September 1993 (1993-09-02) claims 1-4,7 ---	1-16
Y	US 5 834 118 A (WENFANG SHI ET AL) 10 November 1998 (1998-11-10) claims 1,17 ---	1-16
A	WO 97 45474 A (MAANSSON JAN ANDERS EDVIN ;BOOGH LOUIS (CH); PERSTORP AB (SE); PET) 4 December 1997 (1997-12-04) claim 1 --- -/-	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *8* document member of the same patent family

Date of the actual completion of the international search

21 February 2001

Date of mailing of the international search report

28/02/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Niaounakis, M

INTERNATIONAL SEARCH REPORT

Internat. Application No.

PCT/US 00/30556

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PETTERSSON B ET AL: "HIGH-SOLID ALKYDS BASED ON HYPERBRANCHED (DENDRITIC) POLYMERS - A NEW CONCEPT WITH NEW OPPORTUNITIES" PROCEEDINGS OF WATER-BORNE, HIGHER-SOLIDS & POWDER COATINGS SYMPOSIUM, 9 February 1994 (1994-02-09), XP000646275 the whole document</p> <p>-----</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. al Application No

PCT/US 00/30556

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9317060 A	02-09-1993	SE 468771 B AT 165609 T AU 3653093 A CA 2117486 A,C DE 69318295 D DE 69318295 T DK 630389 T EP 0630389 A ES 2115762 T HK 1005487 A JP 2574201 B JP 7504219 T KR 158912 B SE 9200564 A US 5418301 A	15-03-1993 15-05-1998 13-09-1993 02-09-1993 04-06-1998 01-10-1998 07-10-1998 28-12-1994 01-07-1998 08-01-1999 22-01-1997 11-05-1995 15-01-1999 15-03-1993 23-05-1995
US 5834118 A	10-11-1998	SE 503559 C AT 187467 T AU 704344 B AU 3489395 A CA 2198755 A DE 69513840 D DE 69513840 T DK 779908 T EP 0779908 A ES 2140704 T GR 3032356 T JP 10505377 T NO 971061 A PT 779908 T SE 9402994 A WO 9607688 A	08-07-1996 15-12-1999 22-04-1999 27-03-1996 14-03-1996 13-01-2000 27-07-2000 08-05-2000 25-06-1997 01-03-2000 27-04-2000 26-05-1998 30-04-1997 31-05-2000 09-03-1996 14-03-1996
WO 9745474 A	04-12-1997	SE 509240 C AU 2985497 A EP 0902803 A JP 2000511219 T SE 9602019 A	21-12-1998 05-01-1998 24-03-1999 29-08-2000 29-11-1997